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Solvent mediated interactions for the selective recovery of Cadmium from Ni–Cd battery waste

Archana Agrawal *, Pankaj Pathak, D. Mishra, K.K. Sahu

Metal Extraction and Forming Division, NML, Jamshedpur, India

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ABSTRACT

This work deals with the development of a solvent extraction process for the selective separation of cadmium, from cobalt and nickel, using DEHPA as an extractant. After mechanical separation, dissolution of the electrode material in H_2SO_4 and iron removal the leach liquor obtained was subjected to solvent extraction for the extraction and separation of all the three metal ions. The conditions were optimized for the selective recovery of Cd using 20% D2EHPA with 60% saponification. Saturated loading capacity for 20% (60% saponified D2EHPA) was found to be 10.89 g L^{-1} Cd, 1.404 g L^{-1} Ni, and 0.032 g L^{-1} Co at O/A ratio of 1:1. McCabe–Thiele plot at varying O/A ratio indicated the requirement of 4 stages for 100% extraction of Cd at O/A ratio of 1:1.5. The dependence of extraction on pH indicated that the extraction of Cd(II) proceeds according to a cation-exchange reaction at lower acidity and to a solvating reaction at higher acidities. The co-extracted Ni and Co were effectively scrubbed with 50 g L^{-1} $CdSO_4$ at pH 0.5. 99.6% Cd was stripped from the loaded D2EHPA with 75 g L^{-1} of H_2SO_4. Based on the slope analysis of the plots of log D_{Cd} versus log $[(HR)_2]$ and pH vs log $D_{Cd,}$ Cd was found to be extracted as $CdR_2.(HR)_2$. The process seems to be promising for the production of pure metal streams which can further be used to produce valuable commercial products vis-a-vis the environmental protection.

1. Introduction

Secondary batteries such as nickel–cadmium batteries have dominated over the primary types in the electronic world due to several advantages such as charge retention for a larger time, smaller in size hence easily portable and of course rechargeable. However after certain period of its usage, the charge–discharge efficiency of these batteries deteriorates and these batteries are considered to be waste. Disposal of these spent batteries containing cadmium, nickel and cobalt poses a serious environmental problem due to their toxic nature.

Various conventional methods for the disposal of these spent batteries which were used in the recent past involve methods such as landfill disposition, stabilization, incineration and/or recycling processes. Landfill disposition/stabilization of battery residues becomes very expensive due to the increasing amount of waste produced and limited storage capacity of sanitary landfills and/or special waste dumpsites. Incineration of batteries is not encouraged because of huge cost involvement and emissions of toxins such as mercury, cadmium and dioxin into the environment [1]. Therefore, recycling of spent batteries appeared as the most adequate destination for this type of waste. Recycling of wastes is important since it may contribute to the benefit of future generations and preservation of raw materials [2].

Literature survey reveals that both pyro and hydrometallurgical methods were tried for the recovery of metals from wastes containing Ni–Cd batteries and an overview of the current processes including pyrometallurgical and hydrometallurgical routes for the recycling of portable batteries has been published by Bernardes et al. [1], Salgado [3] and Espinosa [4]. Since pyro-methods were found to recover Cd at high temperatures at around 900 °C loosing the Ni and Co values in the slag [5,6], hence other process routs such as hydrometallurgical methods would prove to be a better option where all the three metals could be recovered.

Several papers have reported the hydrometallurgical treatment of several cadmium containing waste materials from the acidic leach solutions/or synthetic solutions containing these metals by solvent extraction route using organophosphorous extractants such as di-2-ethylhexyl phosphoric acid (D2EHPA), (2-ethylhexyl) phosphonic acid mono 2-ethylhexyl ester (PC 88A) and bis(2,4,4trimethyl pentyl) phosphinic acid (Cyanex 272) [6–18]. Bis(2,4,4 trimethyl pentyl) dithiophosphinic acid (Cyanex 301) demonstrated the selectivity for the separation of Cd from Ni–Co in sulfate liquors but the stripping of metal from loaded organic phase was difficult and was possible with high HCl concentration [17]. Di-(2-ethylhexyl)phosphoric acid (D2EHPA) is a commercially used extractant. It has been widely used in liquid–liquid extraction for the separation and purification of liquid effluents containing various metals [19–21]. It was assumed that the extraction of metal ions took place mainly by their reaction with the extractant molecules adsorbed at the interface and not by reaction in the bulk liquid, on account of the high interfacial activity of D2EHPA and its low solubility in the aqueous solution. In addition, it was suggested that the overall extraction rate was mainly controlled by diffusional resistance in the immediate vicinity of the interface [22–24].

* Corresponding author. Tel.: +91 657 2345058; fax: +91 657 2345213.
E-mail address: archana_nml03@yahoo.com (A. Agrawal).

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The present study considers the extraction and separation of Cd(II), Co(II) and Ni(II) from the actual leach solution obtained by leaching the electrode of the Ni–Cd battery in acidic condition with D2EHPA under the optimal conditions in order to selectively separate Cd(II) from Co(II) and Ni(II) present in a mixture.

2. Experimental

2.1. Working solutions and apparatus

Cylindrical shaped Ni–Cd batteries were procured from BEL, Pune. Leach liquor was generated by leaching the electrode material of these spent Ni–Cd batteries containing 40.5% Ni, 23% Cd, 0.8% Co and 13.5% Fe. All other chemicals used in the present study were of AR grade. Di-(2-ethylhexyl) phosphoric acid (D2EHPA), (Fluka, AG, Buchs) was used as an extractant in the present investigation without further purification. The extracting solvent was prepared by dissolving appropriate volume of D2EHPA in distilled (160–200 °C fraction) kerosene oil (diluent) unless otherwise stated, to obtain organic solutions of different concentrations. 5% of isodecanol was added as a phase modifier to ease the phase separation. The pH value of aqueous phase before and after extraction was measured with a pH meter (Systronics μ pH system 362).

Metal analysis was performed by atomic absorption spectrophotometer (Thermo SOLAAR S-2). Mass balance gives the amount of metal extracted by the extracting solvent. The FT-IR spectra of the extractant and their complexes were recorded on an Alpha FT-IR to assess the modes and extent of binding of extractant with Cd.

2.2. Preparation of the leach liquor

Spent Ni–Cd batteries were broken manually and various fractions were separated. 100 g of electrode material of compositions 40.5% Ni, 23% Cd, 0.8% Co and 13.5% Fe was dissolved in 68 ml of H_2SO_4 under oxidizing condition maintained by adding 41 ml of HNO_3 in 500 ml of the leachant at 80 °C. The leach slurry was filtered and collected along with the wash solution. This solution contained sufficient amount of iron hence it was diluted and iron was precipitated by adjusting the pH up to 4.5. The iron free leach solution of compositions (g L^{-1}): 12.45 Ni, 7.3 Cd, 0.212 Co was further used for the selective extraction of Cd using saponified di-2-ethylhexyl phosphoric acid (D2EHPA).

2.3. Extraction experiments

The extraction experiments were conducted with a known amount of D2EHPA of a known concentration dissolved in distilled kerosene (160–200 °C fraction). The appropriate volume of aqueous solution (10 ml) containing metal ion and 10 ml of pre-neutralized D2EHPA at an organic/aqueous phase ratio of 1, were mixed in a separatory funnel and equilibrated for 5 min. All the experiments were carried out at 30 °C. Tests for the extraction of a known amount of Cd(II), Co(II) and Ni(II) mixture were carried out initially with un-saponified 10% D2EHPA but the extraction was not good due to the decrease in pH of the raffinate at equilibrium, hence the solvent was pre-neutralized (saponified) with the stoichiometric amount of 30% NaOH at different percentages, for the maximum extraction of the metal ions. For saponifying the solvent a calculated amount of 30% NaOH was added to the extraction solvent and was mixed homogenously by stirring with a magnetic stirrer till a clear solution was obtained. The concentration of the extracting solvent was selected in such a way that the difference between the yields of extraction of each cation, taken separately is largest (maximum for cadmium and minimum for cobalt and nickel).

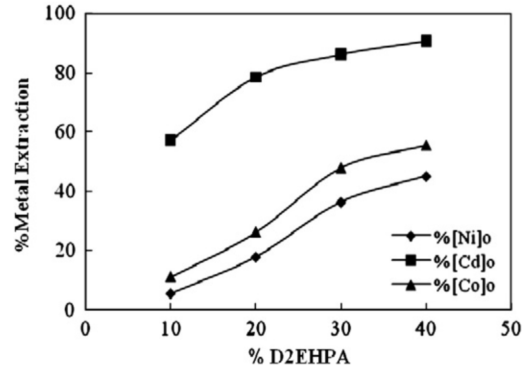

Fig. 1. Effect of solvent concentration on the extraction of Cd, Ni and Co from the leach solution. Initial pH of the aq feed 4.31, T 30 °C, t 5 min, [Aq feed] g L^{-1} 12.45 g L^{-1} Ni, 7.3 g L^{-1} Cd, 0.212 g L^{-1} Co.

3. Results and discussion

3.1. Effect of extractant concentration on extraction of Cd, Ni and Co

The effect of the initial concentration of D2EHPA on the extraction of Cd, Ni and Co from the leach solution of compositions 12.45 g L^{-1} Ni, 7.3 g L^{-1} Cd, and 0.212 g L^{-1} Co respectively was studied in the range of 10–40% (v/v) at O:A ratio of 1 at 30 °C. Since the extracting solvent when used without any saponification showed a poor extractability, it was saponified to 90%. The result showed that with the increase in the concentration of extractant (90% saponified) from 10 to 40%, the extraction percentage of cadmium increases from 50.1% to 95.9%, nickel from 12.7 to 45.12% and cobalt from 10.5 to 52.9% in a single contact (Fig. 1). Separation factors (α_{M2}^{M1}) were calculated for the selectivity of Cd over Ni and Co in the solution and also for Ni in the presence of Co (Table 1).

Although extraction percentage increases with the increase in solvent concentration, separation factor data indicates that selectivity for cadmium over nickel is almost same up to 30% D2EHPA and is slightly higher at 40% DEHPA and cadmium over cobalt increases with the increase in solvent concentration. However separation of Ni from Co is not possible. Since extraction percentage of the metal was around 86.2% for Cd along with 32.85% Ni and 38.76% Co with 20% extractant concentration, further experiments were conducted with 20% solvents unless otherwise stated.

3.2. Effect of equilibrium pH on extraction of Cd, Ni and Co by D2EHPA

Extraction of Cd, Ni and Co by D2EHPA depends on the parameters such as initial pH of the aqueous feed, solution composition and solvent concentration by the formation of various species. In an unsaponified system uptake of metal ions decreases the pH of the aqueous feed therefore the extraction of M^{2+} by D2EHPA can be described by a cation exchange reaction as follows:

$$M^{2+}{}_{(aq)} + n[HR]_2(org) \Leftrightarrow \left[MR_2(HR)_{2(n-2)(org)}\right] + 2\,H^{+}{}_{(aq)} \tag{1}$$

Table 1
Separation factors (α_{M2}^{M1}) for the separation of Cd from Ni and Co and Ni from Co with different concentrations of D2EHPA and 90% saponification.

D2EHPA %	α_{Ni}^{Cd}	α_{Co}^{Cd}	α_{Co}^{Ni}
10	16.05	8.55	0.53
20	23.7	9.97	0.42
30	22.56	14.62	0.65
40	28.33	20.74	0.73

Table 2
Effect of initial concentration of metal in feed solution on equilibrium pH and percent metal extraction.

Saponification % ↓	Solution composition g L^{-1}											
	Solution 1: Ni—18.63, Cd—17.24, Co—1.89				Solution 2 : 12.45—Ni, 7.3—Cd, C0—0.212				Solution 3: Ni—6.69, Cd—3.87, Co—0.11			
	Eq pH	% Extraction			Eq pH	% Extraction			Eq pH	% Extraction		
		Ni	Cd	Co		Ni	Cd	Co		Ni	Cd	Co
20	2.05	4.47	25.4	5.67	1.95	6.79	24.9	6.73	1.55	36.17	79.71	36.7
40	2.45	6.01	58.6	8.9	2.35	15.54	59.2	16.9	1.94	43.58	83.85	50.45
60	2.98	12.02	76.1	17.86	2.61	26.54	81.7	35.5	2.56	64.87	85.71	65.14
80	3.54	15.35	81.5	24.53	2.86	30.32	88.6	36.22	2.68	66.66	94.9	70.64
90	4.34	24.47	93.03	37.31	3.03	35.05	94.6	40.4	2.82	68.46	94.96	71.55

Where M^{2+} represents Cd^{2+}, Ni^{2+} and Co^{2+}, HR is the D2EHPA molecule, n is the stoichiometric coefficient of the extracted complex and (n-2) is the number of additional solvating D2EHPA molecules, aq and org represent the aqueous and organic phases respectively.

Eq. (1) shows that due to the release of H^+ ions into the aqueous solution the pH of the aqueous phase decreases thereby affecting the metal extraction adversely. Thus pH plays a very important role in the extraction of metal which can be maintained by the addition of acid or alkali to the aqueous feed during the extraction process. However addition of acid or alkali externally may lead to some changes in the aqueous phase volume. Hence saponification i.e. pre-neutralization of the organic phase was opted to avoid volume change and maintain the desired pH which could be shown by the following equation

$$Na^+_{(aq)} + \tfrac{1}{2}(HR)_{2(Org)} \longrightarrow ------NaR_{(org)} + H^+_{(aq)}\ldots\ldots \quad (2)$$

Thus for the aqueous feed containing 12.45 g L^{-1} Ni, 7.3 g L^{-1} Cd, and 0.212 g L^{-1} Co with an initial pH of 4.31, the equilibrium pH of the raffinate was found to vary from 1.95 to 3.03 after the extraction of Cd, Ni and Co when the saponification of the extracting solvent was varied from 20% to 90% by treating 20% D2EHPA with stoichiometric amount of 30% NaOH for the required percent saponification (Table 2). The maximum extraction was observed at an equilibrium pH of 3.03 with 90% saponification of D2EHPA, with the initial pH of the aqueous feed of 4.31. Increase in equilibrium pH beyond 3.03 was not possible by further saponification of the solvent. Table 2 indicates that with a 60% saponified extraction solvent, about 81.7% of Cd was extracted, and hence all the further experiments were conducted by using 20% solvent which was saponified to 60%.

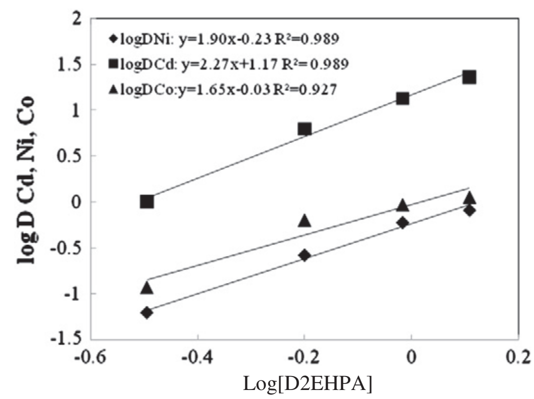

Fig. 2. Plot of Log[D2EHPA] vs logD Cd, Ni, Co. Aq. feed (g L^{-1})—Ni:12.4, Cd: 7.3, Co: 0.212, O/A:1, t: 5 min, T 30 °C.

Table 3
Separation factor values for Cd with respect to Ni, Cd with respect to Co and Ni with respect to Co at varying saponification of 20% DEHPA with 5% isodecanol in kerosene in three solution mixture with varying metal concentration in it.

% Saponification	Eq pH	α^{Cd}_{Ni}	α^{Cd}_{CO}	α^{Ni}_{CO}
Org feed: 20% D2EHPA + 5% isodecanol in kerosene, Aq. feed (g L^{-1}): 18.63 Ni, 17.24 Cd and 1.89 Co (synthetic solution), O/A 1:1, t—5 min, T 30 °C, initial pH—4.6				
20	2.05	15.41	11.99	.77
40	2.45	22.12	14.45	.65
60	2.98	23.3	14.64	.63
80	3.54	24.29	13.56	.56
90	4.35	41.24	22.46	.54
Org feed: 20% D2EHPA + 5% isodecanol in kerosene, Aq. feed (g L^{-1}):12.45 Ni, 7.3 Cd and 0.212 Co (leach liquor), O/A 1:1, t—5 min, T 30 °C, initial pH—4.6				
20	1.95	10.2	10.3	1.013
40	2.35	7.9	7.2	0.86
60	2.61	12.2	8.05	0.62
80	2.86	16.9	12.9	0.55
90	3.03	16.7	13.3	0.67
Org feed: 20% D2EHPA + 5% isodecanol in kerosene, Aq. feed (g L^{-1}): 6.69 Ni, 3.87 Cd and 0.11 Co (leach liquor), O/A 1:1, t—5 min, T 30 °C, initial pH—4.6				
20	1.55	6.01	5.9	0.98
40	1.94	5.4	4.1	0.76
60	2.56	3.3	3.2	0.99
80	2.68	9.3	7.7	0.83
90	2.82	8.7	7.5	0.86

3.3. Effect of initial concentration of the metals in the aqueous feed

Effect of initial concentration of the metals in the aqueous feed was also studied in order to study the effect of saponification on the metal extraction and change in equilibrium pH. Therefore three mixtures with different concentrations of Cd, Ni and Co were used in these experiments. Extracting solvent concentration was kept constant i.e. 20% D2EHPA mixed with 5% isodecanol in kerosene and saponification of this solvent was varied from 20 to 90% with 30% NaOH. Results of extraction percentage of Cd, Ni and Co and the equilibrium pH are given in Table 2.

Result showed that with the increase in percent saponification of the extractant the extraction percentage of metal increased at all

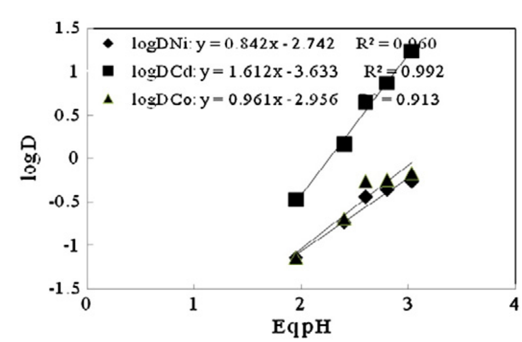

Fig. 3. Plot of Eq pH vs log Cd, Ni Co. Aq. feed (g L^{-1})—Ni:12.4, Cd: 7.3, Co: 0.212, organic phase— 20% D2EHPA + 5% isodecanol in Kerosene, O/A:1, t: 5 min, T 30 °C.

Table 4
$pH_{0.5}$ values $_{for}$ the extraction of Cd, Ni and Co by 20% D2EHPA for three different aqueous feed compositions are given in Table 3.

Solution composition $g\,L^{-1} \rightarrow$	Solution 1: Ni—18.63, Cd—17.24, Co—1.89	Solution 2 : Ni—12.45 Cd—7.3, Co—0.212	Solution 3: Ni—6.69, Cd—3.87, Co—0.11
Eq pH at different saponifications	2.05–4.34	1.95–3.03	1.55–2.82
pH0.5 Cd	2.29	2.19	<1.5
pH0.5 Ni	>4.5	>3.03	2.25
pH0.5 Co	>4.5	>3.03	2.0

the metal concentration range, however equilibrium pH was found to vary depending upon the initial metal concentration. Hence in solution 1 with Ni—18.63 $g\,L^{-1}$, Cd—17.24 $g\,L^{-1}$, and Co—1.89 $g\,L^{-1}$, the pH varied from 2.05 to 4.34, in solution 2 with Ni—12.45 $g\,L^{-1}$, Cd—7.3 $g\,L^{-1}$, and Co—0.212 $g\,L^{-1}$ and solution 3 with Ni—6.69 $g\,L^{-1}$, Cd—3.87 $g\,L^{-1}$, and Co—0.11 $g\,L^{-1}$ the equilibrium pH varied from 1.95 to 3.03 and 1.55 to 2.82 respectively. It was also observed that at any saponification, the percent metal extraction increased with the decrease in initial metal concentration in the aqueous feed. This is due to the availability of more number of active sites on the extracting solvent for the metal ions to attach.

In order to find out the optimum percentage saponification of the extracting solvent, which could give maximum selectivity for Cd with respect to Ni and Co, at any metal concentration as studied by using three solution mixtures, the separation factor values α_{Ni}^{Cd} for Cd w.r.t. Ni and α_{CO}^{Cd} Cd w.r.t. Co were compared (Table 3). Separation factor values showed that for any metal composition as considered in these experiments, Cd was extracted more selectively as compared to Ni and Co. However with the increase in pH value the co-extraction of Co and Ni increased along with the increase in Cd extraction. Extraction percentage values for each metal at varying saponification as given in Table 2, indicated that equilibrium pH of the raffinate after the metal extraction with 60% saponified D2EHPA (20% in kerosene and 5% isodecanol) varied from 2.56 to 2.98 for the three solution mixture with varying metal compositions.

This pH range was found suitable for the selective extraction of Cd. Beyond this saponification, co-extraction of Ni and Co was quite high which would affect the purity of Cd in the scrubbing and stripping stages. Hence all the further experiments were performed with 20% D2EHPA in kerosene with 60% saponification.

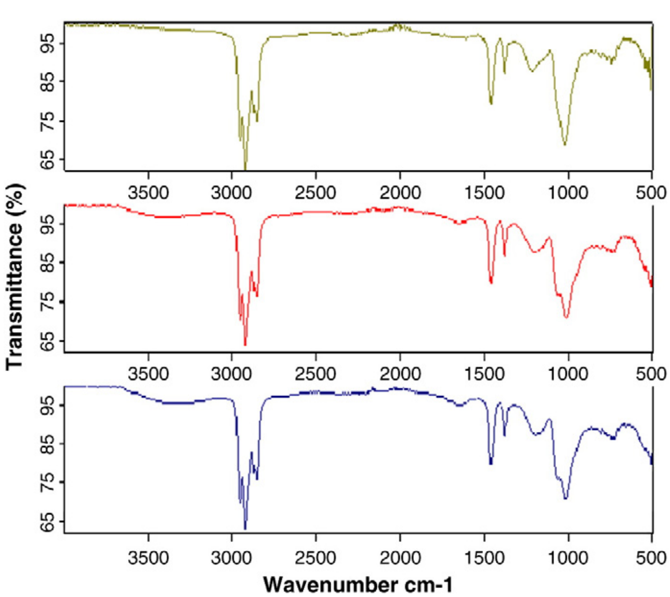

Fig. 4. FTIR spectrum of 20% DEHPA in ID and kerosene (without saponification), with 60% saponification and Cd loaded DEHPA.

3.4. Association of the extracted species during the extraction process

Extraction of a metal by a solvent can either be a cation exchange process or a complex formation process. Various factors were found to affect this extraction process leading to different stoichiometries or involvement of different forms of complexes of metal and the extractant. Thus stoichiometry of the probable extracted species was determined on the basis of slope analysis by plotting Log D versus Log [D2EHPA] (Fig. 2). Where D is the distribution coefficient of Cd, Ni and Co in organic/aqueous phase. The slope values for all the three metal ions were found to be 2.27, 1.9, and 1.65 with R values of 0.989, 0.989, and 0.927 for Cd, Ni and Co respectively, indicating the involvement of 2 moles of solvent per mole of metal ion. Consequently, these metals were extracted as a 1:2 metal/reagent complex from the sulfate medium. It is known that Cd exists as Cd^{2+} in the acidic range and alkyl phosphoric extractants such as D2EHPA are found in dimeric form in aliphatic diluents such as kerosene. These facts and the slope values indicated the formation of $CdR_2.(HR)_2$ type of species which could be shown by the following equation

$$\mathrm{Cd(II)}_{(aq)} + 2(\mathrm{HR})_{2(org)} \Leftrightarrow \mathrm{CdR_2(HR)}_{2(org)} + 2\mathrm{H}^+_{(aq)}\ldots\ldots \quad (3)$$

The above equation gives the following equilibrium constant (K) as

$$K = \frac{[\mathrm{CdR_2(HR)_2}]_{org}.[\mathrm{H^+}]^2_{aq}}{[\mathrm{Cd^{2+}}]_{aq}.[(\mathrm{HR})_2]^2_{org}.} \quad (4)$$

Again distribution of Cd between D2EHPA and aqueous phase is depicted by the following distribution coefficient equation as

$$D = \frac{[\mathrm{CdR_2(HR)_2}]_{org}}{[\mathrm{Cd^{2+}}]_{aq}}. \quad (5)$$

Hence Eq. (4) can be written as

$$K = \frac{D[\mathrm{H^+}]^2_{aq}}{[(\mathrm{HR})_2]^2_{org}}. \quad (6)$$

Taking log of both the sides

$$\mathrm{Log}\,D = \log K + 2\ \mathrm{pH} + 2\ \log[(\mathrm{HR})_2]_{org} \quad (7)$$

Since the studies were performed in the pH range from 1 to 5, the extraction of Cd in this pH range occurred by a cation exchange reaction. A similar fact was observed by Singh and Dhadke in the investigation on the extraction of Ti with D2EHPA/PC-88A at low and high acidity [23] .They obtained a slope value of 2 for the plot of log D vs log [solvent] at low acidity (0.1 M, $HClO_4$) and at high acidity (9.0 M, $HClO_4$), indicating the formation of 1:2 complex of Ti(IV): D2EHPA/PC-88A with the formation of $TiOR_2.2HR$ at low acidity and

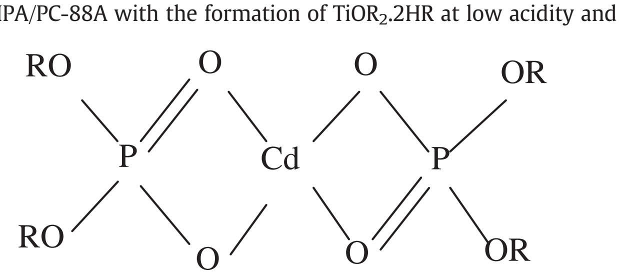

Fig. 5. Proposed structure of the complex of Cd with D2EHPA.

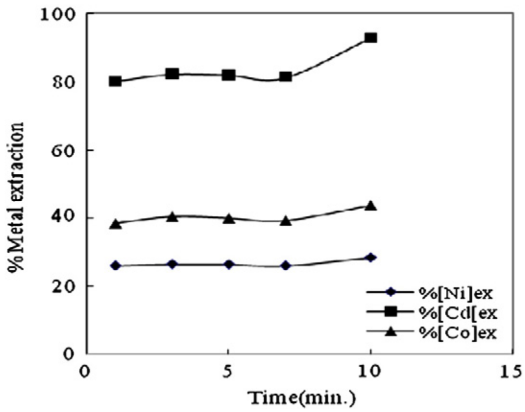

Fig. 6. Plot of Time (min) vs % Metal extraction. Aq. feed (g L^{-1})—Ni:12.4, Cd: 7.3, Co: 0.212, organic phase— 20% D2EHPA + 5% isodecanol in Kerosene, saponification 60%, O/A:1, t: varied, T 30 °C.

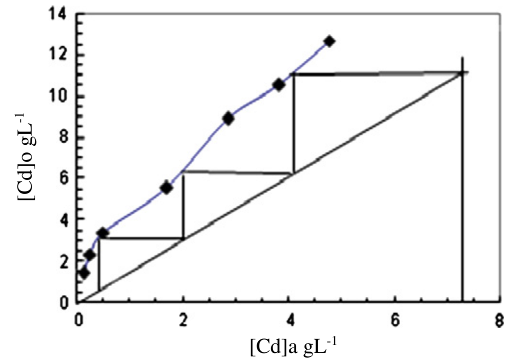

Fig. 8. McCabe–Thiele plot for the extraction of Cd at different O/A ratios.

at high acidities the extraction takes place by solvation reaction, where HR is the extractant D2EHPA and PC-88A in dimeric form [24–26].

A plot of equilibrium pH vs. log D (Fig. 3) was linear with a slope of 1.612, 0.842 and 0.961 with R value of 0.992, 0.960 and 0.913 for Cd, Ni and Co respectively, indicating the exchange of 2 mol of H^{+} ion with 1 mole of Cd(II).

It was further observed that the mechanism of extraction with D2EHPA varies with the experimental conditions. Mellah et al. [25] have used D2EHPA for the recovery of zinc and cadmium from phosphoric acid. The results indicate that the extraction of Cd(II) from phosphoric acid (5.5 M) with the D2EHPA dissolved in kerosene can be explained assuming the formation of the species $CdR_2(HR)_{1/2}$, HR being the active component in the extractant di(2-ethylhexyl)phosphoric acid. Elyahyaoui et al. have proposed the formation of the $CdR_2(HR)_2$ complex with D2EHPA [26].

The efficiency and selectivity of this solvent with respect to the metal ions in the aqueous phase were determined by comparing the $pH_{0.5}$ for the extraction of Cd(II), Ni(II) and Co(II) at 50% extraction which were obtained from the plot of percentage metal extraction at varying equilibrium pH of the raffinate at three different solution compositions (Table 4).

Thus with the decrease in Cd concentration in the aqueous feed from 17.24 g L^{-1} to 3.87 g L^{-1} the pH $_{0.5}$ value decreases from 2.29 to <1.5. For Ni, $pH_{0.5}$ was found at 2.25 for the low concentration of Ni (6.69 g L^{-1}) in the aqueous feed, and when the Ni concentration was 12.44 g L^{-1} and 18.63 g L^{-1} in the aq feed the maximum eq pH attained was 3.03 and 4.5 respectively, with the percent Ni extraction of only 35.26 and 24.5 respectively. Similarly for Co concentration varying from 1.89 to 0.11 g L^{-1} in the aqueous feed, $pH_{0.5}$ was 2.0 at low Co concentration (0.11 g L^{-1}) and for a concentration of 0.21 and 1.89 g L^{-1} of Co in the aq feed the $pH_{0.5}$ value is higher than the maximum equilibrium pH attained during the extraction i.e. 3.03 and 4.5 respectively. This clearly shows the selectivity of this extracting solvent for Cd at low pH value without much interference from the co-existing Ni and Co in the aqueous feed. It was also found that at any particular pH, the percent metal extraction decrease with the increase in the concentration of metal ion in aqueous feed. This fact was also observed by Ritcey and Ash brook [27] and according to them a low metal concentration in the feed solution attains equilibrium at low pH. Hence 20% D2EHPA (60% saponified) was found suitable for the selective extraction of Cd at high metal concentration in the aq feed in the equilibrium pH ranging from 2.35 to 2 9.

Effect of saponification of acidic extractants in a mixed solvent of D2EHPA with 2-octanol in kerosene has been extensively studied by Wu et al. [28–30]. They found that there is a formation of micro-emulsion or reversed micelle, during the conversion of the solvent in the sodium form. When this solvent was used for the metal extraction the micro emulsion droplets or the reversed micelle are destructed. This clearly explains for the water solubilization in the organic diluents observed in the industrial solvent extraction process.

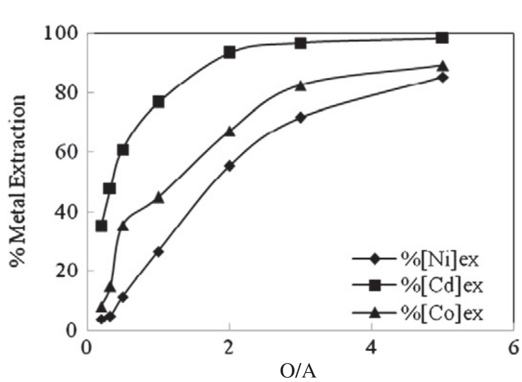

Fig. 7. Effect of O/A on the extraction of metal.

3.5. FT-IR study of cadmium complex

FTIR was applied to identify various vibrational characteristic bands of 20% DEHPA (with 60% saponification) before and after the metal extraction. The FT-IR spectra of 20% D2EHPA in 5% isodacanol diluted in kerosene have been analyzed (Fig. 4) and the results are quite similar to those found by other researchers. Characteristic vibrational bands for D2EHPA i.e. P−O, P−O−C or P−O−H and −OH were identified at 1215, 1022 and 1607.5 cm^{-1}, respectively. These bands were found to be more intense than the bands corresponding to the 2-ethylhexyl moieties (3000–2850, 1460, and 1380 cm^{-1}). The band at 1610 cm^{-1} corresponds to the O–H bending vibration [31]. On interaction of the extracting solvent with any compound, the phosphoryl bond is highly affected. From the FT-IR spectra of the unsaponified 20% D2EHPA, 60% saponified and the Cd loaded organic phase, it was observed that the

Table 5
Scrubbing of co-extracted Ni and Co from the Cd loaded D2EHPA. LO: 1.404 g L^{-1} Ni, 10.89 g L^{-1} Cd, and 0.032 g L^{-1} Co in single contact at O/A = 1/1, t = 5 min.

Scrubbing agent	Scrubbing (%)		
	Ni	Cd	Co
3 g/L H_2SO_4	30.6	3.9	21.32
5 g/L H_2SO_4	44.7	7.85	33.5
6 g/L H_2SO_4	52.0	9.07	40.0
7 g/L H_2SO_4	54.1	12.75	44.6
10 g/L H_2SO_4	66.2	22.4	60.0
10% NH_4SO_4 + 1 g/L H_2SO_4	67.97	20.7	72.97
10% NH_4SO_4 + 2 g/L H_2SO_4	80.32	40.0	87.6

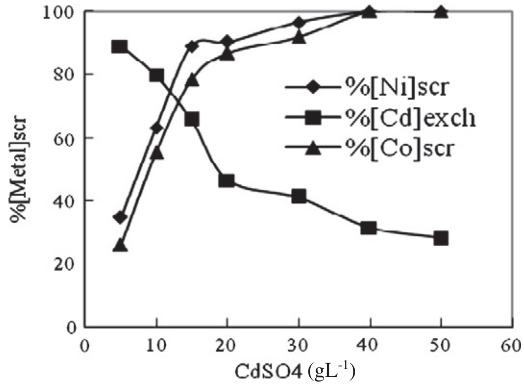

Fig. 9. Effect of $CdSO_4$ concentration on the scrubbing of co-extracted Ni and Co.

D2EHPA as well as its corresponding Cd complex exhibits the characteristics peaks at 2955.06–2854.9 and 1459.5 cm^{-1} for C–H stretching and bending vibrations of –CH_3 moiety, respectively [32,33]. The absence of low intensity characteristic peaks for P–(OH) in the region 2750–2550 cm^{-1} indicated the formation of Cd complexes. The shift in –OH deformation bands with reduced intensity with Cd-extractant complexes provides further evidence in favor of complex formation through phosphorous-hydroxyl group. Marginal shift in characteristic band for P O appeared in the range 1140–1200 cm^{-1}, towards higher frequency also indicated the participation of P–O oxygen in the complex formation through a coordination bond. Based on these observations the interaction between DEHPA and Cd atom in the Cd-DEHPA complex can be depicted as shown in Fig. 5.

3.6. Hydrolytic stability and recycling capacity of DEHPA with this aqueous system

Hydrolytic stability and recycling capacity of a solvent is one of the important factors taken into consideration when the solvent has to be used in the up scaling of the process. The hydrolytic stability of D2EHPA with 0.05 M H_2SO_4 was determined by keeping an unsaponified 20% DEHPA diluted with kerosene in contact with the acid. The required amount of the solvent was drawn from this mixture at a predetermined time interval, it was washed with water and saponified to 60% by the required amount of NaOH and was then contacted with leach liquor containing Cd, Ni and Co at O/A ratio of 1 for 5 min. Analysis of the raffinate shows that percent extraction of Cd, Ni and Co was constant at 81.9, 26.5 and 35.3% respectively. Experiments were also conducted to determine the recycling capacity of the extractants by first loading them with Cd(II) and then stripping with a 100 g L^{-1} of H_2SO_4. The stripped organic phase was regenerated and reused for the next cycle after saponification. Metal recovery in each step was calculated from the amount of Cd(II) extracted by the organic phase in that particular cycle. The results reveal practically insignificant changes in the efficiency of the extraction up to 25 cycles. After this there was only slight variation in extraction justifying the stability of this extractant.

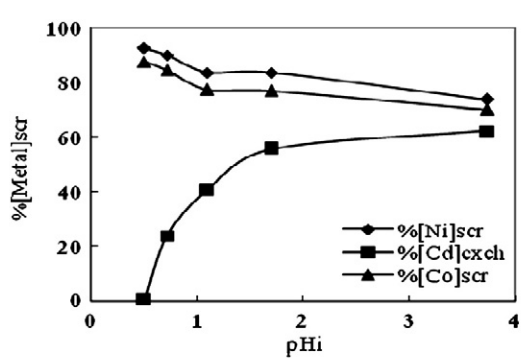

Fig. 10. Effect of initial pH variation of 50 g L^{-1} of $CdSO_4$ on the scrubbing of Co and Ni.

3.7. Effect of shaking time on the extraction of metals by the solvent

Effect of shaking time was studied in order to find out the optimum contact time required by the aqueous and organic phase for maximum metal extraction. Thus 20% D2EHPA with 5% isodecanol in kerosene (60% saponified) was shaken with an aqueous feed containing 12.45 g L^{-1} Ni, 7.3 g L^{-1} Cd, and 0.212 g L^{-1} Co at an initial pH of 4.31 and a sample was drawn at varying time interval from 1 to 15 min. Fig. 6 shows that there is an increase in metal extraction up to 5 min and thereafter becomes constant. Thus shaking for 5 min would be sufficient for maximum extraction.

3.8. Effect of O:A ratio on extraction of Cd, Ni and Co from actual leach liquor

Extraction of Cd, Ni and Co from the leach liquor containing 12.45 g L^{-1} Ni, 7.3 g L^{-1} Cd, and 0.212 g L^{-1} Co, was carried out at different O:A ratios using a 60% saponified 20% (v/v) D2EHPA at initial aqueous phase pH of 4.31 and a temperature of 30 °C, to observe the possibility of extraction of maximum amount of metals in a single contact. It was observed from the result (Fig. 7) that on increasing O:A ratio from 0.2 to 5, the percentage extraction of Cd increases from 34.84 to 99.97%, and for Ni and Co the extraction percentage increases from 3.86 to 85.42% and 7.9 to 89.2% respectively.

An extraction isotherm was obtained by plotting $[M^{2+}]$ g L^{-1} in organic phase and $[M^{2+}]_{aq}$ g L^{-1} in aqueous phase at varying aqueous/organic phase ratio(Fig. 8) which indicated that the extraction was almost quantitative. Data for phase ratio ranging from 5 to 0.2 were fitted to a linear relationship with a very high slope. This figure also shows that, at a chosen O/A (organic/aqueous) volume phase ratio of 1:1.5, the no. of stages required for the extraction of 100% Cd was four.

It was validated by a counter current simulation extraction study. In order to attain the equilibrium, four stage counter current extraction up to 7step was carried out in batch mode at O/A ratio of 1:1.5 with aqueous feed pH of 4.31. Fig. 8 showed that almost a complete extraction of Cd was achieved in the fourth step. Under equilibrium the loaded organic contained 1.404 g L^{-1} Ni, 10.89 g L^{-1} Cd, and 0.032 g L^{-1} Co and raffinate contained 11.5 g L^{-1} Ni, 0.015 g L^{-1} Cd and 0.191 g L^{-1} Co.

The metal loaded organic phase was further subjected to scrubbing of the co-extracted Co and Ni and then the cadmium in the organic phase was stripped by a suitable stripping agent.

4. Scrubbing of loaded organic with Cd, Ni and Co

The loaded organic containing 1.404 g L^{-1} Ni, 10.89 g L^{-1} Cd, and 0.032 g L^{-1} Co was scrubbed using various scrubbing agents such as H_2SO_4(2–10 g L^{-1}), 10% NH_4OH + X g L^{-1} H_2SO_4(X = 1,2) at an O/A ratio of 1:1 at 30 °C. It was found that with the increase in acid concentration used for scrubbing, an appreciable amount (Table 5) of Cd was co-scrubbed along with Ni and Co.

Therefore varying concentration of cadmium sulfate solution was used for the scrubbing of Ni and Co by replacement with Cd.

Concentration of Cd used for scrubbing was varied from 5 to 50 g L^{-1}. It was found that with the increase in $CdSO_4$ concentration the percentage scrubbing of Ni and Co increases from 34.8 to 100% and 26 to 100% respectively, but simultaneously exchange of Cd was also observed from 89 to 28% (Fig. 9). Hence further scrubbing studies were performed by varying the initial pH of 50 g L^{-1} of $CdSO_4$ solution. It was found that with the decrease in pH from 3.92 to 0.5 the percent scrubbing of Ni and Co was 80 to 92.5% and 90 to 100% respectively, along with the decrease in the uptake of Cd from 48 to 0.48% (Fig. 10).

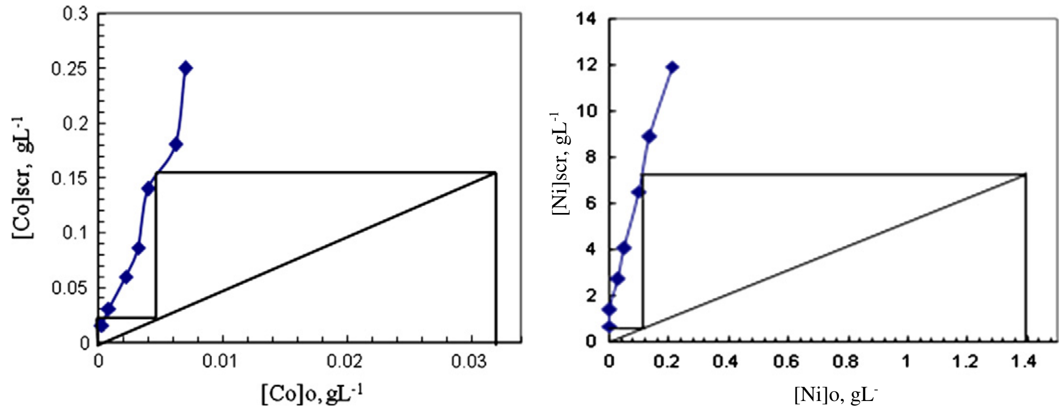

Fig. 11. McCabe–Thiele plot for the scrubbing of Ni and Co at different O/A ratios. Scrubbing agent—50 g L^{-1} $CdSO_4$ solution, metal loaded organic, t—5 min, T—30 °C.

Hence scrubbing of the co-extracted Ni and Co was done by 50 g L^{-1} $CdSO_4$ at pH 0.5. Scrubbing isotherms were plotted to find out the number of stages required for the scrubbing of Ni and Co by plotting [Ni]o vs [Ni]a and [Co]o vs [Co]a at different O/A ratios. Fig. 11 shows that two stages are required for the complete scrubbing of Ni and Co respectively.

5. Stripping of Cd from loaded organic

Stripping of Cd from this loaded organic was performed with varying concentration of H_2SO_4. Fig. 12 shows an increase in Cd stripping from 44% to 83% with the increase in acid concentration from 20 to 75%. So phase variation studies were performed with 75% H_2SO_4 with O/A ratio varying from 1:5 to 5:1. A McCabe–Thiele plot between [Cd]o vs [Cd]aq (Fig. 13) shows the requirement of 4 stages at an O/A ratio of 2:1, for the complete stripping of the cadmium from the loaded organic.

Further a counter current simulation study for stripping was performed in 4 stages in 7 steps. It was found that 99.5% of Cd was stripped in the 5th step after which it was constant. Thus the overall flow sheet for the cadmium recovery from spent Ni–Cd electrolyte is depicted as follows. A process flow sheet for the cadmium extraction by D2EHPA is given as in Fig. 14.

6. Conclusion

In this work a solvent extraction process for the selective separation of cadmium, from cobalt and nickel was developed, using D2EHPA as extractant. After breaking the spent Ni Cd battery manually all the parts were mechanically separated. The electrode material was leached in a solution of H_2SO_4 in an oxidizing atmosphere to bring Cd, Ni, Co and iron into the solution. Iron was removed from the aqueous feed and this iron free solution was subjected to solvent extraction for the extraction and separation of all the three metal ions. Various parameters were studied for the selective separation of all the three metals using various solvents. To start with Cd was selectively recovered by using D2EHPA solution and the raffinate containing Co and Ni was used for the separation and recovery of Co from Ni. Results show that percent extraction of metal increases with the increase in equilibrium pH. At a fixed saponification the percent extraction of Cd, Ni and Co increases with the increase in solvent concentration. Saturated loading capacity for 20% (60% saponified D2EHPA) was found to be 10.89 g L^{-1} Cd, 1.404 g L^{-1} Ni, and 0.032 g L^{-1} Co at O/A ratio of 1:1. With the increase in O/A ratio from 0.2 to 5, Cd extraction increases from 54.65 to 99.4%, Ni and Co extraction percentage increases from 4.8 to 34.5% and 19.7 to 37.5% respectively. McCabe–Thiele plot shows the requirement of 4 stages for 100% extraction of Cd at O/A ratio of 1:1.5. At low acidity D2EHPA was found to be more selective for Cd as compared to Ni and Co. The extraction of Cd(II) proceeds according to a cation-exchange reaction at lower acidity and to a solvating reaction at higher acidities. Extraction and separation of Cd(II) using D2EHPA may be commercially viable as this extractant exhibits a good hydrolytic stability and can be regenerated and utilized (>10 times) for the same purpose without compromising the efficiency of the metal recovery. The co-extracted Ni and Co was effectively scrubbed with 50 g L^{-1} $CdSO_4$ at pH 0.5. 99.6% Cd was stripped from the loaded D2EHPA with 75 g L^{-1} of H_2SO_4. The process seems promising allowing the production of pure metal streams from which valuable commercial products can be produced along with the environmental advantages over the classic pyrometallurgical processes leading undoubtedly to a more efficient management of nickel–cadmium wastes.

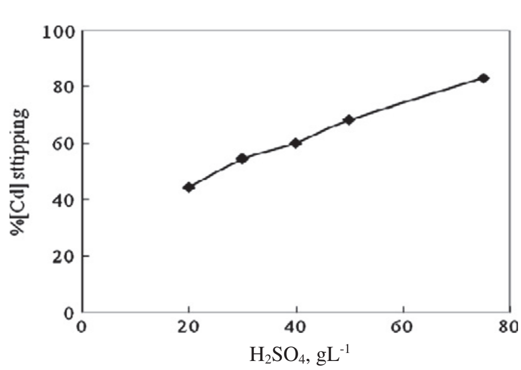

Fig. 12. Effect of H_2SO_4 concentration on the stripping of Cd from the loaded organic.

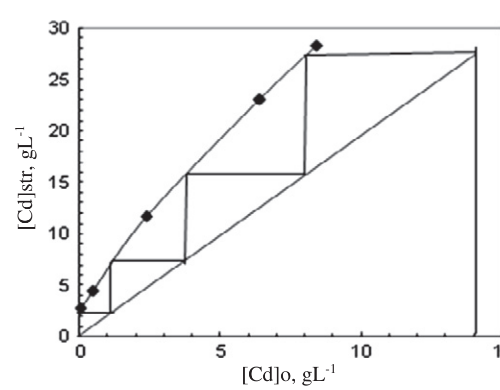

Fig. 13. McCabe–Thiele plot for the Stripping of Cd from loaded D2EHPA.

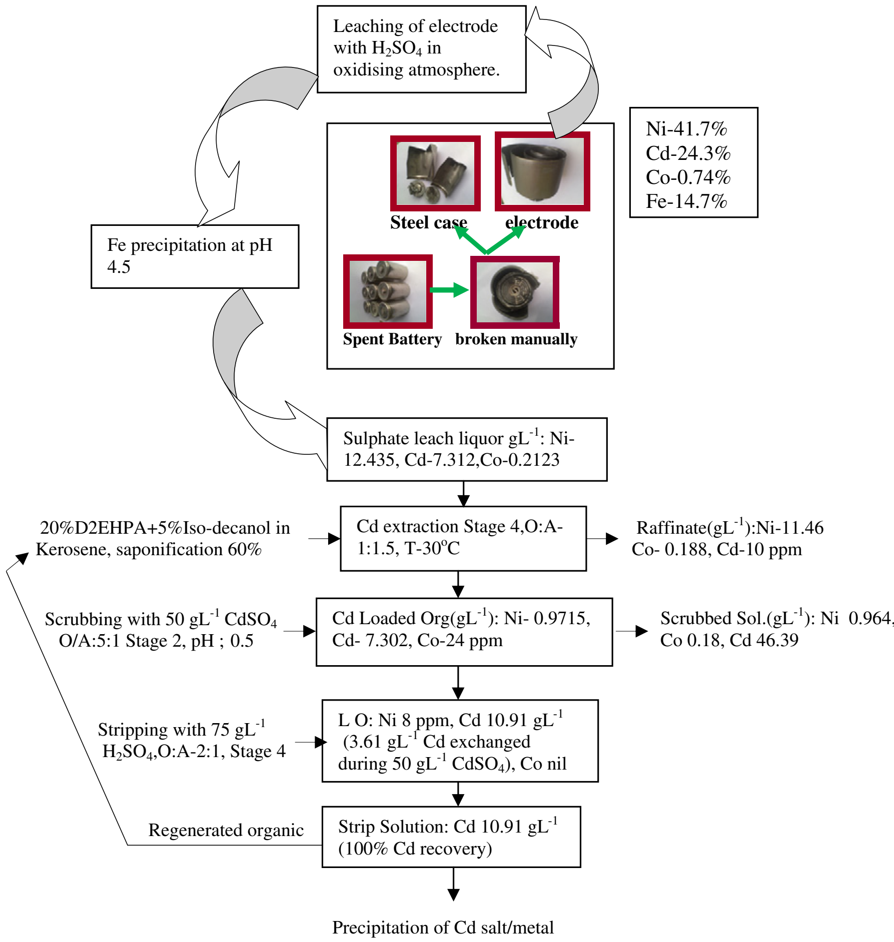

Fig. 14. A pictorial flow sheet for the extraction of Cd by 20% D2EHPA.

Acknowledgments

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